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Response to First Office Action

The following comments are offered in response to the first office action dated January 13, 2005 for Application No. 10/090,034 filed March 5, 2002 titled Conversion of Petroleum Residua to Methane.

1. Claims 1-8 were rejected under 35 USC 103(a) as being unpatentable over Soung, US Patent No. 4,459,138 in view of Leas, US Patent No. 5,855,631 and in further view of Koh, et al, US Patent No. 4,094,650.

   Regarding Claim 1, Soung discloses a process for the production of methane from carbonaceous solids comprising alkali metal mixtures from about 3 to 50% (therefore less than about 50%) of such compounds added to the feed (C4/L 8-12). The corresponding disclosure of Koh, et al, teaches from about 5 to 50% of alkali metal constituent added to the feed (C7/L 41-43). However, the alkali metal content (more than 30% and less than 50%) recited in Claim 1 of the present invention refers not to the feed but to the solids in the gasifier. The disclosures of Soung and Koh, et al, cited above relate to Claim 4 of the present invention, which recites added alkali metal compound of less than 1% of the feed. On this basis the disclosures of the prior art teach away from the present invention, which lists as one objective **[0012]** a means of contacting feed with catalyst that reduces catalyst usage by more than 95%.

   Regarding the gasifier solids composition recited in Claim 1 of the present invention, one skilled in the art would recognize that the composition of the solids in the gasifier differs substantially from the composition of the feed because most of the carbonaceous material would have been gasified. The teaching of the prior art regarding the composition of the solids in the gasifier is given only qualitatively by Soung, but the patent of Koh, et al, discloses (C 17/L 1-7) 19.6% carbon, 0.2% hydrogen, 0.3% oxygen, 1.2% sulfur, 32.3% ash, 23.2% sodium carbonate, and 23.2% potassium carbonate. In the terminology of Claim 1 of the present invention, coke would refer to the carbon, hydrogen, oxygen, and sulfur of the Koh, et al, patent,

a total of 21.3%, far less than the recitation of Claim 1 requiring more than 50% coke. Further, the alkali metal content cited by Koh, et al, allowing for the alkali metal content of their carbonates, amounts to a total of 23.2% of the gasifier solids, significantly less than the requirement of more than 30% and less than 50% recited by Claim 1 of the present invention. The disclosure of Koh, et al, which relates to the requirement of less than 10% other inorganic constituents recited by Claim 1 of the present invention comprises the disclosed 32.3% ash plus the carbonate content of 23.2%, a total of 55.5%. Consequently, every component of the gasifier solids disclosed by the prior art is far outside and teaches away from the recitation of Claim 1 of the present invention.

With regard to the requirement of the mass flow rate of steam of 1.8-2.0 times the mass flow rate of feed recited in Claim 1 of the present invention, the rejection cites the Koh, et al, disclosure of the solids loading in the injection gas (C 11/ L 11-17) of 0.2-5 pounds solid feed to actual cubic foot of injection gas. This citation refers to the volumetric (not mass) requirement of injection gas for pneumatic transport of the feed into the gasifier. In the disclosed embodiment of Koh, et al, the injection gas is a portion of the total steam and recycle gas fed to the gasifier. To determine the mass flow rate of steam relative to feed, one skilled in the art would find that the Koh, et al, patent discloses (C 11/ L 52-54) a total of 0.09 mole of steam and recycle gas per pound of solids fed, the steam comprising 63.3 mole per cent of the total. Thus the ratio of steam to solids fed is 0.057 mole steam per pound of solids fed, or 1.03 pounds steam per pound of feed. This disclosure teaches away from the mass ratio of 1.8-2.0 recited by Claim 1 of the present invention.

None of the cited references nor any combination discloses or provides guidance with respect to the hourly mass flow rate of feed relative to the mass of alkali metal in the gasifier recited as 0.3 to 0.6 in Claim 1.

The novel and non-obvious recitations of Claim 1 are thus the composition of the gasifier solids, the mass ratio of steam to feed, and the hourly mass flow rate of feed relative to the mass of alkali metal in the gasifier.

The other recitations of Claim 1 are the feed preheat temperature range, composition of the steam and recycle gas, the range of operating temperatures and pressures, withdrawal of the raw gas product, recovery of methane, and recycle of hydrogen and carbon monoxide. These recitations are all well known in the prior art and are included to limit the scope of the claim to the present invention.

Regarding Claim 2, the rejection cites the disclosure of Soung to withdraw solids from the gasifier to recover alkali metals from the residue, the recovery being the objective of the Soung invention. However, one skilled in the art, seeking to eliminate the need for catalyst recovery as an objective of the present invention **[0012]**, would not be drawn to the Soung disclosure for guidance on controlling the rate of solids withdrawal. Claim 2 of the present invention is limited by the range of gasifier solids compositions recited in Claim 1 and requires control of the

composition by both solids withdrawal from the gasifier and catalyst addition to the gasifier.

Claim 3 is withdrawn in view of the persuasive citation of the rejection.

Regarding Claim 5, the term "stages" is clearly identified in the disclosure of the present invention as meaning separate fluidized beds, each consisting of a dense phase of fluidized particles having a controlled depth and supported by a grid, and each having a dilute phase or disengagement zone above the dense phase. The dilute phase is not a separate stage. Thus the cited disclosure of Soung (C 5/ L 10-15) constitutes a single stage in the terminology of the present disclosure.

Regarding Claim 6, the rejection cites Soung (C 5/L 18-31) and Fig. 1, identifying line 45 as a standpipe. The solids discharge line from the bottom of a cyclone separator is commonly referred to as a dipleg and is so identified in both the Soung patent and the disclosure of the present invention. A standpipe as described in the disclosure of the present invention is a means of controlling the level of solids in a fluidized bed by capturing excess solids in an overflow well at the top of the standpipe and allowing the overflowing solids to discharge at the bottom. Cyclone separators with diplegs are disclosed but not claimed in the present invention. The purpose of the cyclones and diplegs in the disclosures of both the Soung patent and the present invention is to capture fine solid particles which are entrained in the dilute phase and return them to the dense phase fluidized bed. This incidental circulation of fine solid particles occurs at an uncontrolled rate and is undesirable but necessary to maintain the solids inventory in the bed. Likewise, line 37 in Fig. 1 of the Soung patent is cited by the rejection as a riser. A riser in the terminology of the present invention and in common terminology of the art of fluidized solids is a means of pneumatically conveying a controlled rate of solids flow upward by means of aeration and lift gas at sufficiently high velocity to entrain substantially all of the solid particles. Line 37 in the Soung patent is not a riser but is the gasifier outlet corresponding to Line 22 in Fig. 1 of the present invention, the function of which is to convey all of the raw product gas out of the gasifier.

Regarding Claim 7, the rejection cites the disclosure of Soung (C 4/ L 22-28) device 26 as an aerated riser. Device 26 of the Soung disclosure is a star wheel feeder or similar device, which regulates the solids feed rate into a stream of carrier gas to a manifold for distribution to the feed nozzles. The recitation of Claim 7 of the present invention refers to the means of contacting fresh feed with the gasifier solids by injecting into the aerated riser, whereas in the disclosure of Soung and that of Koh, et al, fresh feed is introduced directly into the fluidized bed gasifier. One skilled in the art would note that the teaching of Soung and Koh, et al, if modified to feed liquid petroleum residua would be consistent with the industry practice of fluidized bed coking, wherein the feed is injected directly into the fluidized bed, and would not be motivated to do otherwise. The disclosure of the present invention teaches that the distribution of the feed over the gasifier solids is improved by injection into the

aerated riser as opposed to relying on the turbulence of the fluidized bed to mix fresh feed with the gasifier solids.

2. Claim 4 is rejected under 35 USC 103(a) as being unpatentable over Soung, US Patent No. 4,459,138 in view of Leas, US Patent No. 5,855,631 in further view of Koh, et al, US Patent No. 4,094,650, and in further view of Adsetts, US Patent No. 3,926,584. The novel and non-obvious recitation of Claim 4 is the requirement of less than 1% alkali metal compound added to the feedstock. As noted in paragraph 1 above, the disclosures of Soung and Koh, et al, teach away from this recitation.

   The disclosure of Adsetts refers to conversion of hydrocarbon boiling at less than 350 C or methanol as feedstocks over a catalyst comprising nickel, alumina, and minor amounts of alkaline earth and alkali metal compounds(C 1/ L 39-45). The cited composition of 0.25 – 0.75% is the proportion of alkali metal compound in the catalyst (not the feed) preferred when the feed is hydrocarbon as opposed to methanol. In this process, the vaporized feed is typically mixed with steam and passed over a fixed bed of catalyst. The active component of the catalyst is nickel, and it was found that the addition of the alkaline earth and alkali metal components prolonged the catalyst life. If one attempted to feed petroleum residua boiling higher than 565 C, the resulting coke deposition on the catalyst would lead to a sudden and catastrophic flow stoppage.

3. Claim 8 is rejected under 35 USC 103(a) as being unpatentable over Soung, US Patent No. 4,459,138 in view of Leas, US Patent No. 5,855,631 in further view of Koh, et al, US Patent No. 4,094,650, and in further view of Lomas, US Patent No. 4,541,923.

   The Lomas patent discloses the well-known practice in the art of catalytic cracking of circulating freshly regenerated catalyst at a rate of 5-10 times the feed rate in an aerated riser. The comparison of this feature of the present invention with the practice of catalytic cracking is documented in the present disclosure in paragraph **[0038]**:

   > "...Although there are similarities between this method of introducing feed to the method of feeding commonly practiced in catalytic cracking, the reasons for doing so are not obvious. In catalytic cracking, feed is introduced into the riser to mix with freshly regenerated catalyst. Essentially all the feed is vaporized and the vapor phase components undergo the cracking reactions by contacting the acid catalyst surface. All of the desired reaction takes place within a few seconds in the riser and the reaction is terminated by separating the catalyst from the product vapor at the end of the riser. In the present invention, only a negligible part of the catalytic reaction takes place in the riser. The purpose of adapting the catalytic cracking feed method to the present invention is to distribute the petroleum coke formed in the initial thermal decomposition uniformly over the catalytically active solids for later gasification in the two stages of fluidized beds. Indeed the

standard practice for feeding petroleum residue to fluidized beds for other purposes, such as fluidized bed coking, is to inject the feed directly into the fluidized bed, relying on the bed turbulence to distribute the coke throughout the reactor."

One skilled in the art would recognize that the catalyst to oil mass ratio (5-10) in the riser of a catalytic cracking process is used to control the severity of the reaction. In catalytic cracking, higher catalyst to oil ratios increase the temperature and the exposure of the vaporized feed to freshly regenerated catalyst, leading to increased reaction severity. The reaction severity of the present invention is determined by the process conditions recited in Claim 1, and is insensitive to the mass ratio of solids to feed in the riser. Given that the nature of the problem to be solved by the present invention is not control of reaction severity, but improved distribution of feed on the gasifier solids, one would not be motivated to specify the mass ratios taught by catalytic cracking. The range of mass ratios required by the present invention must provide a large excess of solids relative to feed to prevent agglomeration and bogging such as sometimes occurs in fluidized bed coking when feed is injected directly into the fluidized bed, and there is insufficient bed turbulence to adequately mix the fluidized solids with the liquid feed. It is therefore coincidental that the mass ratios used in catalytic cracking partially overlap the range of 5-20 recited in Claim 8, and in fact the preferred ratio of 10 disclosed in the embodiment of the present invention is at the high end of the catalytic cracking range.

4. Claim 9 is rejected under 35 USC 103(a) as being unpatentable over Soung, US Patent No. 4,459,138 in view of Leas, US Patent No. 5,855,631 in further view of Koh, et al, US Patent No. 4,094,650, and in further view of Skaggs, US Patent No. 5,628,623.

The rejection notes that both Soung and Koh, et al, teach that entrained fines in the raw product gas may be captured in cyclone separators and conveyed back to the fluidized bed through the cyclone diplegs. This means of maintaining solids inventory is a standard industry practice for fluidized beds in general. The particles are discharged by gravity from the bottom of the dipleg into the fluidized bed. The bottom of the dipleg is normally equipped with a swinging plate known as a trickle valve which allows solid particles to trickle into the bed without permitting gas from the fluidized bed to flow back up the dipleg.

Jet ejectors as disclosed by Skaggs are well known means of fluid pumping even for fluids with entrained particulates. One skilled in the art might thus have found it obvious to combine the two disclosures and couple a jet ejector with the bottom of a dipleg as a gravity assist for the purpose of discharging the collected fine particles back into the fluidized bed, and a means of preventing gas from the fluidized bed to flow into the dipleg.

However the problem to be addressed is not an improved means of returning fine particles to the fluidized bed, but rather the stated objective in paragraph **[0016]** of

the present application of controlling the size distribution of the particles. Specifically, it is desired to increase the size of the finest particles which are generated by gasification and attrition. The novel and non-obvious disclosure of the present invention employs the jet ejector for conveying them to a point where they flow past the feed injection nozzles, thereby being coated with fresh feed which will deposit a layer of petroleum coke on each particle, increasing its size. No disclosure in any of the references nor any combination suggests this solution to the problem of increasing the size of the finest particles.

5. Claim 10 is rejected under 35 USC 103(a) as being unpatentable over Soung, US Patent No. 4,459,138 in view of Leas, US Patent No. 5,855,631 in further view of Koh, et al, US Patent No. 4,094,650, and in further view of Skaggs, US Patent No. 5,628,623, and further view of Machado et al., US Patent No. 6,506,361.

The rejection asserts that it is obvious to combine the teachings of the first four references with the Machado disclosure specifying a superficial liquid velocity of 0.05 to 1.0 meters per second in the reactor downstream of the discharge of the jet ejector. The corresponding zone of the present invention is the aerated riser where the superficial gas (not liquid) velocity is about 6 meters per second.

Machado teaches that these liquid flow rates are necessary to obtain high rates of mass transfer with the monolithic catalyst in the reactor. However the present invention does not involve liquid mass transfer. Rather the superficial velocity range recited in Claim 10 of the present invention refers to the gas velocity in the dipleg on the inlet (not the discharge) side of the ejector, and the problem to be solved is not mixing or mass transfer as implied in the rejection, but rather to ensure the flow of solid particles down the dipleg so as not to overflow into the cyclone where they would be entrained into the plenum and the gasifier outlet.

Given the nature of the problem, there is no reason for one skilled in the art to consider the Machado disclosure.

Conclusion

In summary, the cited prior art severally and in combination teaches away from the present invention and does not address the stated objectives. One of ordinary skill in the art would not be drawn to the cited combinations, which if applied would in some cases result in an inoperable system. All of the claims are novel and non-obvious, with the exception of the withdrawn Claim 3. The withdrawal of Claim 3 and the subsequent renumbering of claims and references results in the following revised Claims 3-9:

3. The process of Claim 2 wherein said alkali metal compound is dispersed as a fine powder admixed with said petroleum residue feedstock at a concentration of less than 1% by mass, maintained in suspension by

agitation, and injected into said reactor with said preheated injected feedstock.

4. The process of Claim 1 wherein said reactor consists of two or more stages with respect to said upwardly flowing gaseous mixture, and wherein said fluidized particles are circulated between stages.

5. The process of claim 4 wherein said fluidized particles are circulated from upper to lower stages by means of one or more standpipes, and are circulated from lower to upper stages by means of one or more aerated risers.

6. The process of claim 5 wherein said preheated feedstock is injected into at least one aerated riser.

7. The process of claim 6 wherein the mass flow rate of solids in the aerated riser is between 5 and 20 times the mass flow rate of said injected feedstock.

8. The process of claim 6 wherein said gaseous product mixture is withdrawn through at least one pair of cyclone separators in series, said series consisting of a primary cyclone separator discharging into the inlet of a secondary cyclone separator, each cyclone separator being equipped at the bottom apex of its conical section with a pipe dipleg to discharge the collected fine particles separated from said gaseous product mixture, and wherein the dipleg of the secondary cyclone separator discharges into a collection zone coupled to the inlet of a jet ejector, and wherein said jet ejector discharges the collected fine particles into the riser below the level of feedstock injection.

9. The process of claim 8 wherein said jet ejector is operated with sufficient motive fluid to induce a downflow of gas and entrained solids in said dipleg of said secondary cyclone separator, said gas and solids to proceed downwardly with a superficial velocity of more than 0.1 meter per second and less than 1 meter per second.

Based on the foregoing comments, Applicant asserts that with claims revised as above, the application is ready for allowance.

Respectfully submitted,

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